

Electrochemical detection of 14 common munitions constituents

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Abstract Electrochemical detections of 14 munitions constituents (MCs) listed on the Environmental Protection Agency hazardous waste list were examined using square wave voltammetry. Of the MCs that showed peak resolution in the scanned range, the reduction potential, limit of detection and limit of quantitation are reported here. The MCs tested are in three groups: nitrobenzenes, nitrotoluenes, and other nitro-aromatics: tetryl, HMX, and RDX. There was a correlation between peak resolution and the number of nitro groups for the nitrobenzenes and nitrotoluenes. The nitro group distance from the methyl for the nitrotoluenes with two nitro groups showed some correlation to the ability to detect as well. Some mixture experiments were conducted in which MCs with three and two nitro groups were detected simultaneously. While tetryl readily displayed two peaks, RDX and HMX did not show such clear peak resolution.

Keywords Electrochemical detection · Munitions constituents · Square wave voltammetry

1 Introduction

Long-term monitoring (LTM) of waste disposal sites for munitions constituents (MCs), using the Environmental

Protection Agency Method 8330A, high-performance liquid chromatography, is a costly analytic technique for which currently there is no comparable alternative [1]. LTM cost projections for the Army, Navy, Air Force, and Department of Energy are in the order of hundreds of millions of dollars [2]. LTM requirements apply to disposal sites, production sites, and training locations and do not stop after remediation and closure of military bases [3]. This growing governmental expense has inspired research and development of low-cost techniques to detect MC concentrations in ground water in parts per billion [2, 3]. Since the cost of the current method is mostly due to transportation of samples, the focus has been to conduct research in areas that show promise of an in situ device [2, 4]. At the same time, due to increase in military operational tempo, the demand for commercial production of munitions in the many forms such as propellants, pyrotechnic, and primary and secondary explosives has grown. Locations for production, regular use, and disposal have become more limited over these years due to closure of Department of Defense base [5, 6]. This has increased concentrations of munitions and their chemical by-products in the soil and ground water in military training areas. With the need for a cost-effective alternative to be established, some background to the LTM program is included to report the provisions by which an alternative method may be developed.

All ammunition products used by the Department of Defense as defined by RCRA become solid waste upon use during the course of military training. As some of the materials are deemed unrecoverable on the training site, these areas are subjected to LTM based on solid-waste remnants of munitions. LTM is continued on training areas in conjunction with military operations. As a means to measure the amount of MCs affecting the environment in

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these areas, the Environmental Protection Agency mandated concentration quantitation limits for testing based on Method 8330A, high-performance liquid chromatography with ultra violet detection. Sampling of ground water and use of an approved laboratory for testing is a means to detect the 14 MCs listed in Table 1 in concentrations on the order of parts per billion [7, 8]. Ultimately, this is the accepted method for detection of MCs.

It is well known that method 8330A is costly and slow in terms of transportation of samples, sample preparation, and instrumentation [2]. Method 8330A also requires advanced laboratory technical skills for analysis. Likewise, the quantitation limits associated with Method 8330A are a recommended standard, thus leaving the door open for development of other technologies to replace it, so long as new developments operate with the same precision [9].

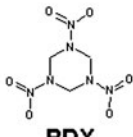
In light of the need to cut costs of LTM and flexibility to pursue alternate methods, the Environmental Laboratory of the U.S. Army Corps of Engineers Research and Development Center in Vicksburg, Mississippi continues

to conduct research on sampling, separation, and detection of MCs with a goal of a low-cost, fast, specific, light-weight, in situ method that performs with comparable precision to Method 8330A [10]. There are a number of methods under current review, which show promise of separation and detection of MCs [4, 11–14]. While none of them has been able to surpass the current detection limits with adequate precision for all 14 MCs, they have provided motivation for use of electrochemical methods [4, 11–14]. Electrochemical devices have an advantage of minimal measurement times and are integrable into computer systems, although there may be a tradeoff for resolution for field operations from what is observed with HPLC [12].

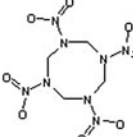
The EPA regulation required LTM for the MCs displayed in Table 1 showing a summary of the EPA low and high limits of detection using Method 8330A and a comparison with concentrations reported for well water in the vicinity of an abandoned ammunition plant. In some cases, the amount of MC found in the ground water largely surpasses the EPA high level limit, while in others, the MC

Table 1 EPA list of MCs as well as summary of ground water samples from ERDC-EL

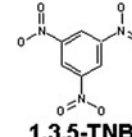
Munitions Constituents (MC)						
Abbreviation	Analyte	EPA Low	EPA High	*Ground Water		
		Level Limit ($\mu\text{g/L}$ -ppb)	Level Limit ($\mu\text{g/L}$ -ppb)	Concentrations 16 May 2007		
				Well 104	Well 105	Well 108
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	-	13.0	2478	528	51
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	0.84	14.0	16262	3248	1085
1,3,5-TNB	1,3,5-Trinitrobenzene	0.26	7.3	10898	2321	783
1,3-DNB	1,3-Dinitrobenzene	0.11	4.0	346		
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	-	4.0			
NB	Nitrobenzene	-	6.4			
2,4,6-TNT	2,4,6-Trinitrotoluene	0.11	6.9	6728	402	828
4-Am-DNT	4-Amino-2,6-dinitrotoluene	0.060	-		25	25
2-Am-DNT	2-Amino-4, 6-dinitrotoluene	0.035	-	221	37	623
2,4-DNT	2,4-Dinitrotoluene	0.020	5.7	408	52	53
2,6-DNT	2,6-Dinitrotoluene	0.31	9.4			
2-NT	2-Nitrotoluene	-	12			
3-NT	3-Nitrotoluene	-	8.5			
4-NT	4-Nitrotoluene	-	7.9			



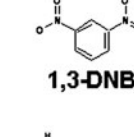
RDX



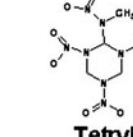
HMX



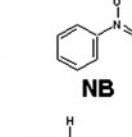
1,3,5-TNB



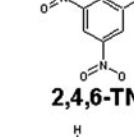
1,3-DNB



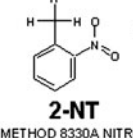
Tetryl



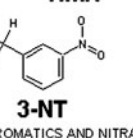
NB



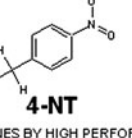
2,4,6-TNT



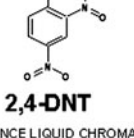
2-NT



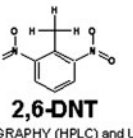
3-NT



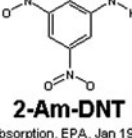
4-NT



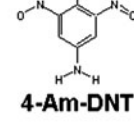
2,4-DNT



2,6-DNT



2-Am-DNT



4-Am-DNT

1. METHOD 8330A NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) and UV absorption. EPA, Jan 1998
 2. ERDC-EL, Vicksburg, Mississippi

was below the detectable range. This follows from the typically using of MCs.

This article summarizes the first reported systematic study of the feasibility of facile monitoring of the 14 common MCs reported by the EPA. We used standard square wave voltammetry (SWV) methods and previously disclosed methods of -modifying gold electrodes to suppress background current [18]. We studied all 14 compounds. We have demonstrated success with 6 MCs using SWV with a normalization and background subtraction approach.

2 Experimental

2.1 Chemicals

MC ampoules, 1000 $\mu\text{g/mL}$ in acetonitrile, were obtained from Cerilliant of Round Rock, TX, USA. Samples for analysis were prepared by dilution of the as-obtained solutions in 0.5 M sodium chloride or 0.1 M phosphate buffer (PB), pH 7. PB was prepared from appropriate combination of monobasic and dibasic sodium phosphate (Fisher). Because the MC analyte was provided as a solution in acetonitrile, it was desirable to fix the acetonitrile concentration during measurement, irrespective of the dilution factor used. Accordingly, acetonitrile (HPLC grade, Honeywell) was added to maintain a concentration of 1:100 v/v acetonitrile:water throughout the experiments. As needed, hydrochloric acid and sodium hydroxide (Fisher) were used for pH adjustments. All alkanethiols were obtained from Sigma–Aldrich, and included methyl-terminated 1-hexanethiol, 1-decanethiol, and 1-dodecanethiol, in addition to hydroxyl-terminated 3-mercapto-1-propanol (MCP), 6-mercapto-1-hexanol (MCH), 11-mercapto-1-undecanol (MCU), and 11-amino undecanethiol hydrogen chloride (AUH). All chemicals were used as received.

2.2 Apparatus and procedure

Square wave voltammetric measurements were carried out on a $\mu\text{Autolab III/FRA 2}$ potentiostat from Brinkman using an E4 series change tip gold disk insert (5.0 mm OD \times 4.0 mm thick, polished) working electrode. The experiments used a silver/silver chloride reference electrode with a 3 M sodium chloride reservoir (Ag/AgCl/3M NaCl RE; BASI) and a platinum wire counter electrode. All potentials are reported relative to the Ag/AgCl/3M NaCl reference. The rotator was from Pine Instruments of Raleigh, NC, USA. Experiments were carried out at a rotation speed of 500 rpm.

Prior to measurement, the working electrode was mechanically polished with 600 and p4000 grit silicon carbide paper from Leco Corps and Buehler, followed by polishing with one micron ultrafine diamond polish on a 1 μm ultrapolishing pad from BASI. After mechanical polishing, the electrode was rinsed with methanol and then deionized water. The electrode was next placed in a 0.1 M sulfuric acid bath, and the potential was cycled for 20 scans ranging from 0 to 1.54 V using a 100 mV/s scan rate. This procedure produces a reproducible initial state of the electrode surface [15]. Following this electrochemical treatment, the electrode was again rinsed with deionized water. For measurements at a bare Au electrode, the prepared working electrode was directly placed into MC-free PB or NaCl electrolyte for conditioning. Alternately, the working electrode was modified with an alkanethiol monolayer. SAM modification was carried out by exposing the electrode to a solution containing 0.1 mM alkanethiol [16, 17]. In the case of MCU, it was dissolved in ethanol rather than deionized water. The reaction times allowed for the formation of the SAMs varied. For the longer chain hydrocarbons, MCU, the electrode was left in the alkanethiol solution for 10 h.

The working electrode (either bare or with a SAM) was first conditioned in solution without MCs using five square wave voltammetric scans at 15 Hz, 4.05 mV step height, and 25 mV amplitude. For bare Au electrodes, the potential range was from 0 to -1.2 V. For electrodes modified with an alkanethiol layer, the potential range was decreased from 0 to -0.7 V for MCP, from 0 to -0.8 V for MCH, and from 0 to -0.9 V for MCU and dodecanethiol. Following this conditioning, a final SWV scan was performed to serve as a background trace. Next, an aliquot of MC solution was added. After 1 min of mixing, a square wave voltammetric scan was carried out. This procedure was then repeated over a series of stepwise additions of MC solution, increasing the concentration of TNT or DNT each time. Error bars, when shown, are one-standard deviation from the mean value.

Because some results are still an order of magnitude away from the EPA high level contamination concentrations for MCs, the capabilities of measuring MCs were tested more systematically in the range of 0–120 ppb. For each of the single analyte experiments, the sensitivity, limit of detection (LOD), and limit of quantitation (LOQ) were estimated by performing ten identical experiments for each analyte concentration. For each square wave voltammogram, the peak current was recorded, averaged, and then used in the LOD and LOQ calculation. The LOD is defined to be three times the standard deviation of the peak current at the lowest detectable concentration divided by the slope of the peak current versus concentration regression line, and the LOQ is defined as 10 times the standard deviation divided by the same slope as similarly described by Gustavo [9]. In each case, it was found

that by discarding the first scan, the reproducibility of the measurement was greatly improved, suggesting that electrode preconditioning should be part of the sensing methodology. Subsequent scans, after the initial discarded scan, were used to calculate the average peak current and standard deviation.

As previously observed, a source of drift in the sensor was related to an increasing baseline current [18]. By developing a correlation based on the difference between peak current I_p measured where a peak was observed, and baseline current I_b , measured at -0.1 V, the LOD and LOQ could be improved. The variation of signal current, $I_s = I_p - I_b$ with potential is then reported for each MC. Based on measurements of the sensitivity, the LOD and LOQ were estimated [9]. The LOD and LOQ were generally found in the ppb range. This is close to the range of

previous work by Wang using a carbon fiber working electrode [19]. These LOD and LOQ values are near the high contamination EPA levels listed above. The EPA low contamination levels are about two orders of magnitude less in most cases. Reliable quantitation of MCs across the entire range of interest, spanning from 0.01 to 10 ppb, may therefore require a preconcentration stage.

3 Results and discussion

SWV was performed on 14 MCs, and clear peaks with a peak height dependent on concentration were obtained for 6 MCs. Figures 1, 2, 3, 4, and 5 show representative results for the categories of MCs tested. The potential sweep was

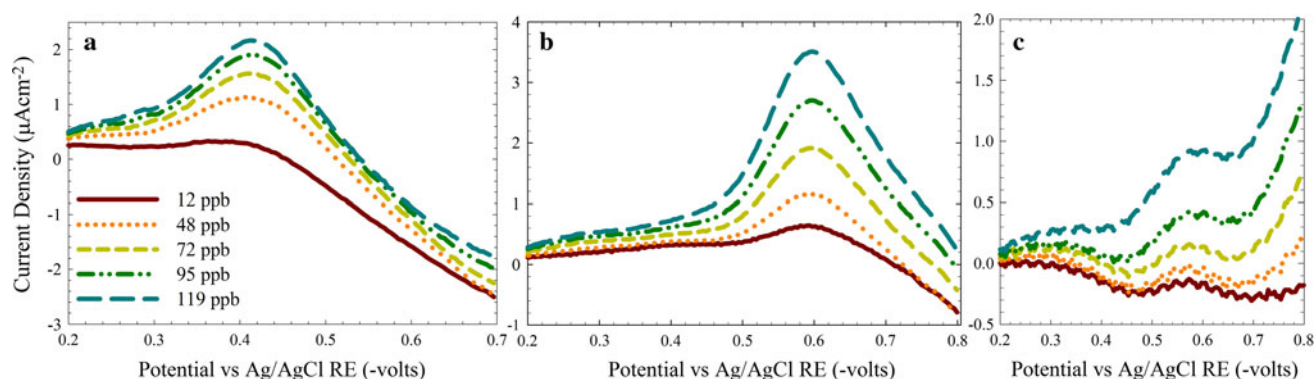


Fig. 1 1,3,5-trinitrobenzene, 0.5 M NaCl (a), 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25$ °C. LOD = 30 ppb, LOQ = 100 ppb. 1,3-dinitrobenzene (b), 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with

MCU = working electrode, pH 7, $T_{avg} = 25$ °C. LOD = 7 ppb, LOQ = 22 ppb. Nitrobenzene is shown in figure (c) with a slight peak at -0.55 V. Only a sample of square wave voltammograms of the experiments conducted is shown here in order to provide clarity to data. Concentrations from 12 to 119 ppb were tested

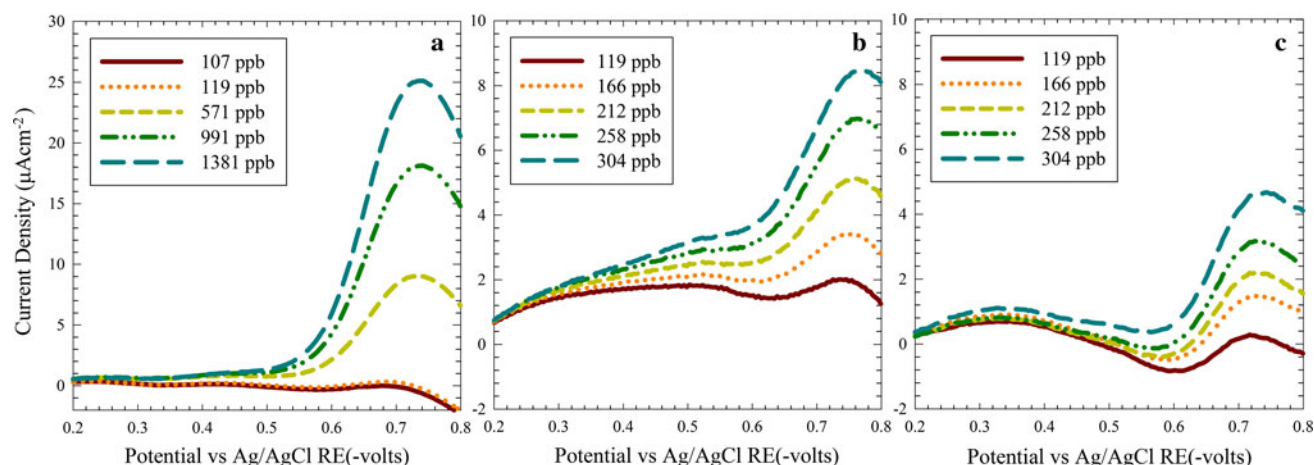


Fig. 2 Representative average SWV for detection of 2,6-dinitrotoluene (a), 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25$ °C. A reduction peak is observed at -0.75 V. Solutions containing 2-Amino-dinitrotoluene (b) show a slight peak at -0.75 V, and 4-Aminodinitrotoluene (c) showed a slight peak at -0.8 V. In

each case, average square wave voltammograms for normalized and background subtracted data are shown. The working electrode was Au with MCU. Only a sample of square wave voltammograms of the experiments conducted is shown here to provide clarity to data. Concentrations from 12 to 1381 ppb were tested

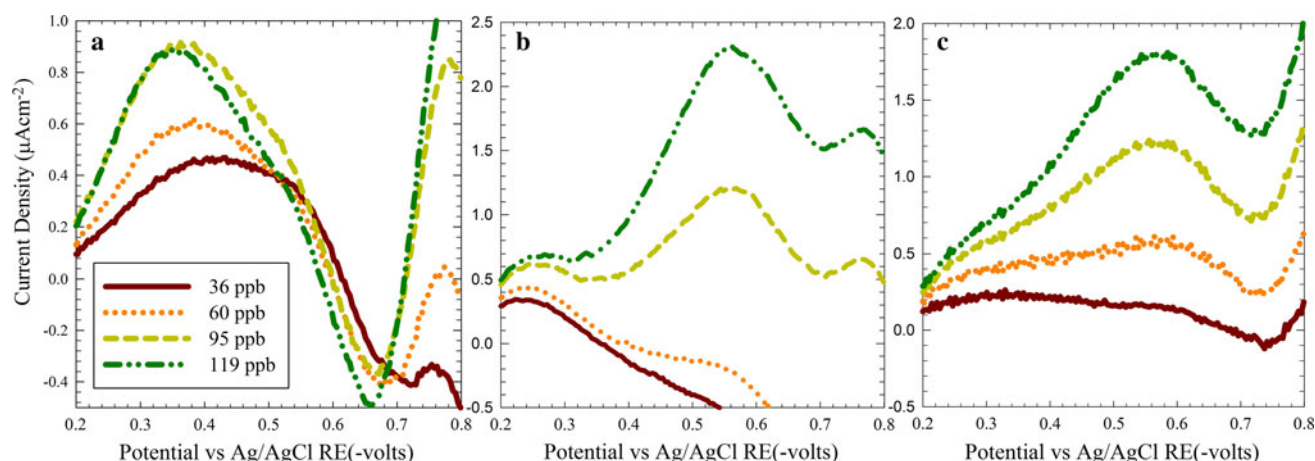


Fig. 3 Representative average square wave voltammograms from solutions containing 4-nitrotoluene (**a**), 3-nitrotoluene (**b**), and 2-nitrotoluene (**c**). Average square wave voltammograms are shown in Fig. 4a with a slight peak at -0.8 V. In figures **b** and **c**, a slight peak at -0.55 V was observed. In each case, the average current is for a square wave voltammogram, normalized and background

subtracted. The working electrode was Au with MCU. Results for larger additions were dropped to improve resolution for current at lower concentrations. Only a sample of square wave voltammograms of the experiments conducted is shown here provide clarity to data. Concentrations from 12 to 119 ppb were tested

generally limited to a range of 0 to -0.8 V in order to preserve the condition of the surface based on the presence of the SAM. Typically increased variability in the signal was observed with scans beyond -0.8 V. In all cases, the average square wave voltammograms for normalized and background subtracted data are shown. The working electrode was Au with MCU. The last addition at a much higher concentration was not included in this plot to improve resolution.

The list of 14 MCs can be further subdivided into categories related to the structure and the number of nitro groups and then electrochemical detection. Of the MCs tested during this study the following subcategories were formed: nitrobenzenes, nitrotoluenes, and other nitroaromatics. Breaking down the MCs within each subcategory as related to electrochemical detection follows.

3.1 NitroBenzenes

For the nitrobenzenes, the peak resolution is readily observed for trinitro benzene and 1,3-dinitrobenzene. For nitrobenzene there is an increase in current over a slightly broader region, but not as precisely defined peak observed. This is similar to the results observed by Bratin for nitrobenzenes [21].

3.2 Nitrotoluenes

For the nitrotoluenes: 2,4,6-trinitrotoluene (three nitro groups) and 2,4-dinitrotoluene (two nitro groups), detection limits were described in previously published work [18]. In the case of 2,6-dinitrotoluene, there was some peak

resolution and a clear increase in current at relatively higher concentrations. The 2-amino-dinitrotoluene displayed an increase in current over a broad region, but not a precisely defined peak. The experiments for 4-amino-

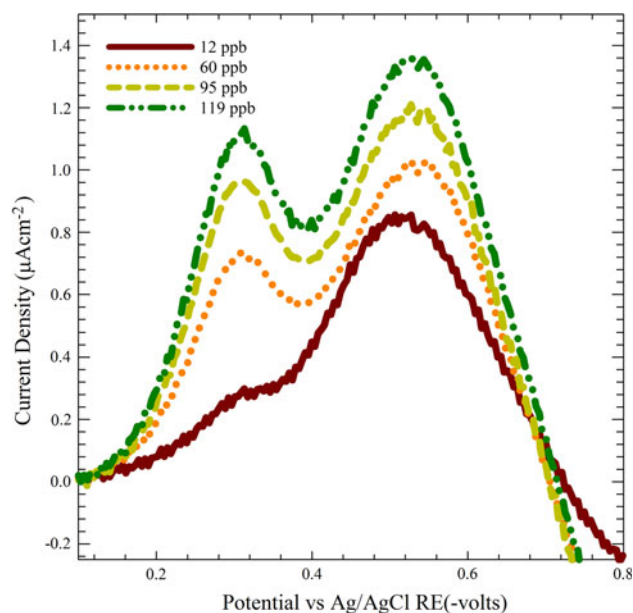


Fig. 4 Tetrayl, 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25$ °C, LOD = 15 ppb, LOQ = 50 ppb. The average square wave voltammograms for normalized and background subtracted data are shown. Two peaks were observed. The working electrode was Au with MCU. Only a sample of square wave voltammograms of the experiments conducted is shown here to provide clarity to data. Concentrations from 12 to 119 ppb were tested

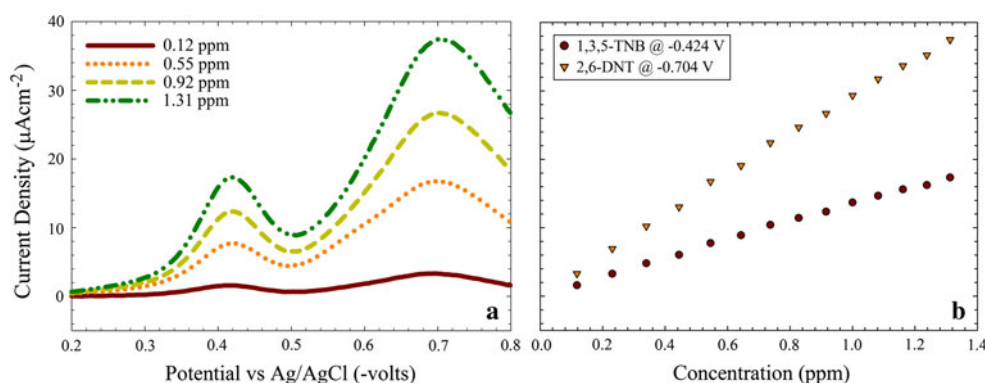


Fig. 5 1,3,5-TNB and 2,6-DNT mixture (a), 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25^\circ\text{C}$. Peak Current Density for 1,3,5-TNB and 2,6-DNT mixture vs concentration (b), 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing,

RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25^\circ\text{C}$. The background has been subtracted from the data. Only a sample of square wave voltammograms of the experiments conducted is shown here to provide clarity to data. Concentrations from 0.12 to 1.31 ppm were tested

Table 2 Summary of results. The previously published work can be found at Bozic et al. [18]

Munitions Constituent	Number of nitro groups	Detection
Nitrobenzenes		
1,3,5-trinitrobenzene	3	Able to detect (ATD)
1,3-dinitrobenzene	2	ATD, peak potential more negative than 1,3,5 TNB
Nitrobenzene	1	Nitro group, increase in current over a broad region, but not a precisely defined peak observed
Nitrotoluenes		
2,4,6-trinitrotoluene	3	ATD, previously published work
2,4-dinitrotoluene	2	ATD, previously published work
2,6-dinitrotoluene	2	ATD at high concentrations, Not counted in the percentage of ATD
2-amino-dinitrotoluene	2	Increase in current over broad region, but not a precisely defined peak observed
4-amino-dinitrotoluene	2	Increase in current over a broad region, but not a precisely defined peak observed
4-nitrotoluene	1	Increase in current over a broad region, but not a precisely defined peak observed
3-nitrotoluene	1	Increase in current over a broad region, but not a precisely defined peak observed
2-nitrotoluene	1	Increase in current over a broad region, but not a precisely defined peak observed
Other nitroaromatics		
Tetryl	4	ATD, 2 peaks observed
HMX	4	Increase in current over a broad range, but not a precisely defined peak
RDX	3	Increase in current over a small range, but not as clearly defined peak as other 3 nitro group aromatics

dinitrotoluene had similar results to 2-amino-dinitrotoluene.

For single nitro group nitrotoluenes, 4-nitrotoluene, 3-nitrotoluene, and 2-nitrotoluene, there was an observed increase in current over a broad region, but not a precisely defined peak.

3.3 Other nitroaromatics

Tetryl, HMX, and RDX have different molecular structures. Consistent peaks were not observed for HMX and

RDX. Results are shown for tetryl in Fig. 4. Two clear peaks in the ranging from 0 to -0.8 V were observed. RDX, perhaps the most common MC after TNT, was not amenable to SWV analysis. However, the initial results from this study indicate that linear changes in peak current due to RDX are possible in the pap range using a gold electrode by SWV and ACV methods. SAM surface modification enhanced peak specificity of RDX. By passivating the background currents at this potential on a modified electrode, reduction peaks and consistent reduction currents at ppm to mM RDX concentrations were

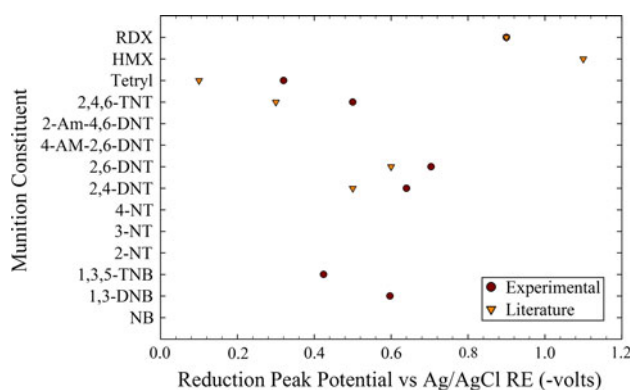


Fig. 6 Experimental conditions 0.5 M NaCl, 1:100v/v acetonitrile:water, 1 min mixing, RDE = 500 rpm, Au with MCU = working electrode, pH 7, $T_{avg} = 25^{\circ}\text{C}$. For MCs with more than one reduction peak, only the first reduction peak potential of the square wave voltammetric sweep is listed here. Literature values from Bratin et al. [21]

observed. With the addition of a preconcentration stage, an electrochemical device may be able to provide an alternative to the existing LTM efforts.

As previously observed with TNT and DNT, MCs that have a potential difference of 0.1 volt and greater were detected simultaneously [18]. In Fig. 5, the SWV results from 1,3,5-TNB and 2,6-DNT show a linear increase in current and consistent peak potentials. Based on these results, we suspect that detection may be possible for two and three nitro group MCs of similar structure.

From the list of 14 MCs, a comparison based on the ability to detect in each subcategory was made and is summarized in Table 2. Generally, the greater the number of nitro groups the greater the probability of detection. For the other nitro-aromatics, there was no clear evidence of detection for RDX and HMX, despite each having three nitro groups.

Figure 6 shows the electrochemical peak potential for the first reduction peak observed as well as values published in articles about detection of MCs [20]. For all of the MCs considered to be experimentally detectable, the peak observed was close to what was found in Bratin's work [21]. Often, sufficient separation in peaks is observed that mixtures can be detected simultaneously as was done in a previous study for DNT and TNT, and as is shown in Fig. 5 for TNB and 2,6DNT [18, 22].

4 Conclusions

Electrochemical Detection of 14 MCs listed on the EPA hazardous waste list was examined using SWV. Of the MCs that showed peak resolution in the scanned range, the reduction potential, LOD and LOQ, were determined. The

MCs tested were in three groups: nitrobenzenes, nitrotoluenes, and other nitro aromatics that make up the EPA list [1]. The peak resolution showed a correlation for the number of nitro groups for the nitrobenzene and nitrotoluene MCs. The nitro group distance from the methyl group for the nitro toluene MCs, showed some correlation to the ability to detect as well. Some mixture experiments were conducted in which three and two nitro MCs were simultaneously detected. While tetryl readily displayed two peaks, RDX and HMX did not show a clear peak resolution at ppb concentrations.

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